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DIVISION OF THE  
STATE GEOLOGICAL SURVEY  
M. M. LEIGHTON, *Chief*  
URBANA

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REPORT OF INVESTIGATIONS—NO. 169

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MICROANALYSIS OF ORGANIC COMPOUNDS  
CONTAINING FLUORINE

BY

HOWARD S. CLARK AND O. W. REES



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MANUSCRIPT COMPLETED AUGUST 1953

## ORGANIZATION

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# MICROANALYSIS OF ORGANIC COMPOUNDS CONTAINING FLUORINE

BY

HOWARD S. CLARK\* AND O. W. REES

## INTRODUCTION

ILLINOIS has been endowed with generous deposits of high-grade fluorspar ( $\text{CaF}_2$ ), one of the prime source materials for fluorine, which is finding increasingly important uses today. To extend the uses of fluorine and thus expand the market for fluorspar, the Geological Survey undertook studies which have increased our knowledge of fluorine chemistry and discovered potentially useful applications for organic fluorine compounds.

To provide adequate analytical data, needed to assure the success of these studies, a microanalytical laboratory was established ten years ago in the Division of Analytical Chemistry of the Geochemical Section. This laboratory, both of necessity and by choice, was used for selecting, modifying, and developing new methods of analysis for fluorine-containing com-

pounds. This report is the result of a decade of experience.

Part I of this report describes methods for fluorine and halogen determinations with particular emphasis on multiple halogen compounds. Part II discusses methods for determining carbon, hydrogen, nitrogen, and sulfur in organic fluorine compounds. A table at the end of the report tabulates typical results obtained by the methods described.

## ACKNOWLEDGMENTS

The writers wish to acknowledge the cooperation of E. D. Pierron and D. R. Dickerson for their help in establishing certain details of procedure, especially in Step 3, and for obtaining part of the analytical results. To F. H. Reed and G. C. Finger, appreciation is expressed for furnishing samples on which to test the procedures described and for helpful suggestions in the preparation of the manuscript.

\*Present address, The Clark Microanalytical Laboratory, Urbana, Illinois.

## PART I

### MICRODETERMINATION AND DIFFERENTIAL ANALYSIS OF THE HALOGENS AND FLUORINE

The analysis of combinations of closely related members of one chemical family has always been an intriguing and at the same time a difficult assignment. The four members of the halogen family have been classical in this respect, and the present interest in organic substances containing two or more of this family has accentuated the need for a precise scheme of analysis for use in routine work.

The literature is rich in research reports dealing with the analysis for one halogen in various combinations of two of the members. These reports usually resulted from a specific need, and therefore it is not surprising that the methods are not generally applicable.

Actually, there are considerable differences in chemical behavior between members of this family and so much difference in the case of fluorine that it has become customary to refer to "the halogens and fluorine." This distinction by terminology is both necessary and desirable.

The methods of analysis and of differentiation used in this laboratory are presented in this report, and therefore it serves several purposes. First, the inevitable improvements are described which have been made since this method of determining fluorine was first reported.<sup>2</sup> Second, the versatility of the equipment is demonstrated by showing that it may also be used in determining the other halogens, in some cases concurrently with the fluorine. Finally, there is shown a means of using the obtainable information to arrive at the percentage of each member of the family in any combination with the others.

Recognizing the fact that most contemporary workers in the field are well-schooled in the more common manipulations, no attempt is made to describe them in de-

tail; however, where they are important, certain modifications are indicated.

In this work, the variations in chemical behavior within the family have been used to make the differentiations. For example (Step 1), fluorine does not combine with silver in the same way that the other members of the family do; therefore, if the combustion products of an organic substance are passed over a silver gauze roll under controlled conditions, the other halogens will be sequestered, leaving the fluorine free to be absorbed and determined by an acid-base titration.

Concurrently (Step 2), the total percentage of the other halogens may be determined gravimetrically from the gain in weight of the silver gauze roll. At this point the other halogens are unidentified.

An argentometric determination (Step 3) is not affected by fluorine under the proper conditions, and will give the weight of silver which combines with the halogens present.

A separate determination of iodine (Step 4) may be made iodometrically by taking advantage of the ease with which it is oxidized to iodic acid.

By the proper interpretation of the information obtained in the various steps, a simple mathematical calculation (Step 5) makes the complete differentiation possible. As each step is precise in its own right, the over-all combination of them is equally precise.

#### STEP 1—DETERMINATION OF FLUORINE

The combustion method of determining fluorine used in this laboratory was reported in 1951.<sup>2</sup> Since then constant use has revealed certain desirable changes which were then made.



## METHOD

Basically this determination depends upon the combustion of the sample with oxygen in a quartz tube. The fluorine is converted into silicon tetrafluoride, which is swept from the tube, absorbed in water, and the hydrofluoric acid produced by the resulting hydrolysis is titrated with standard alkali. In contact with borosilicate glass, some of the fluorine appears to form a boron-fluorine combination which has three fluorine atoms combined with one boron atom, possibly as monohydroxyfluoroboric acid ( $\text{HBF}_3\text{OH}$ ).<sup>2</sup> This fluorine is not released under the usual titration conditions but is obtained through a second titration after the addition of a polyhydroxy compound, as in the titration of boric acid.

## EQUIPMENT

Furnace (B) capable of maintaining a temperature up to  $1200^\circ\text{C}$ . (See figure 1.)

Auxiliary furnace (C) which will accommodate the  $\text{F } 10/18$  junction of the combustion tube and the receiver. The temperature required is  $400^\circ$  to  $550^\circ\text{C}$ .

Microcombustion tube (D), fused quartz, A. C. S. specifications,<sup>3</sup> but with a  $\text{F } 10/18$  outer joint formed on one end without constriction.

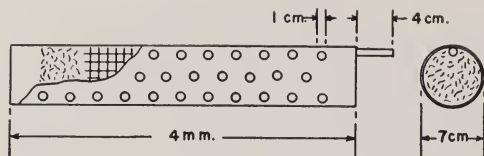


FIG. 2.—Platinum cylinder.

Grote-type borosilicate glass receiver (E)<sup>18</sup> with  $\text{F } 10/18$  inner joint and spray trap (F).

Burette, reservoir type, 5 ml. capacity, at least 0.050 ml. graduations. (The inside of the reservoir and the immersed portion of the burette should be paraffin coated unless the glass is boron-free.)

pH meter with glass and calomel electrodes.

Platinum gauze.

Platinum cylinder (fig. 2) or gauze.

A customary oxygen purification train and pressure regulator (A).

## REAGENTS

Mannitol, reagent grade.

Sodium hydroxide, 0.01N, carbonate-free and boron-free.

Platinum for contact catalysts.

Silver gauze or ribbon.

Quartz chips.

## COMBUSTION TUBE FILLING

Platinum contact stars, which have been freshly etched with aqua regia and well rinsed with distilled water but not ignited,

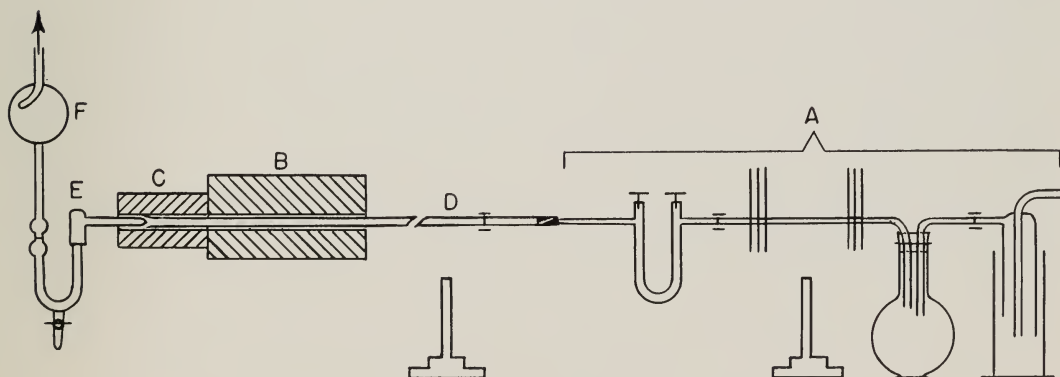


FIG. 1.—Combustion train.

are positioned in the center of the principal furnace section of the combustion tube. The section is completed by filling in both ends to the limits of the furnace with quartz chips; the chips are held in position with freshly etched squares of platinum gauze, at both the entrance and exit. At the entrance end, the platinum gauze should extend well into the combustion section.

#### PROCEDURE

If halogen other than fluorine is present, silver gauze or ribbon (see Step 2), packed in the perforated platinum cylinder or rolled in platinum gauze, is inserted into the auxiliary furnace section. To avoid overheating, it should not extend more than two-thirds of the way toward the principal furnace, thus leaving a buffer zone of at least three centimeters. With the principal furnace (B) at 900°C. (see Remarks, p. 9) and the auxiliary furnace (C) at 400-425°C.,<sup>14</sup> the Grote-type receiver (E,F), properly filled with distilled water, is inserted loosely into the outer joint of the combustion tube, where it will expand rapidly for five minutes, after which time a tight connection can be made safely. The vacuum and oxygen flow are adjusted to allow about one surge per second through the receiver U-tube with an oxygen pressure of about 5 to 7 inches (12.5 to 17.5 cm.) of 50% sulfuric acid. This provides a rate of flow of about 60 to 70 cc. of oxygen per minute.<sup>18</sup> A high-oxygen ratio is required.<sup>15</sup>

Solids are introduced in platinum boats, and liquids are introduced in the usual weighing pipettes made of heat-resistant glass. A sample which will give acid equivalent to 7-10 ml. of 0.01N alkali (3 to 10 mg.) appears to be adequate. The capacity of the silver to remove other halogens, being limited to about 5 or 6 mg.

without recleaning, often may be a limiting factor.

The sample is burned as in any combustion determination, allowing 15 to 20 minutes for the combustion; then the train is flushed for 10 minutes to assure complete transfer of the combustion products.

After the sweeping, the joint connecting the combustion tube (D) and the receiver (E) is shifted out of the auxiliary furnace, without interrupting the oxygen flow. After cooling slightly, the joint will part easily because of the difference in contraction.

The contents of the receiver are transferred<sup>18</sup> to a 100 ml. beaker with cool, freshly boiled distilled water and titrated immediately with 0.01N sodium hydroxide using a pH meter having a glass-calomel electrode system. Under our conditions, plotting  $V$  (volume of titrant) against  $\Delta \text{pH}/\Delta V$ , the initial end point appears at pH 6.7. When this is reached the receiver is rinsed repeatedly into the beaker until the transfer is complete, adjusting to pH 6.7 after each rinsing. The volume of alkali used to this point is recorded as the "initial increment." Continuing the titration, alkali is added rapidly to pH 8.3 (established by plotting as above), approximately 0.5 g. of mannitol is added, and the system again is adjusted to pH 8.3 to complete the titration. The difference between the final volume and the initial increment is the "mannitol increment."

#### CALCULATIONS

A titration blank of 0.075 ml., which represents the amount of alkali necessary to raise the blank system from pH 6.7 to pH 8.3 under our conditions, appears to be necessary. This is deducted from the mannitol increment and the calculation becomes:

$$\frac{[(\text{Initial Increment}) \text{NaOH} + 3 (\text{Mannitol Increment} - 0.075) \text{NaOH}] (\text{N}) (\text{Mil. eq.}) (100)}{\text{Sample Weight}} = \% \text{ F}$$

## INTERFERENCES

Silver is added to the combustion tube filling so that the other halogens or sulfur will not interfere with the fluorine determination.<sup>2</sup> If other halogens but no sulfur are present, the silver should be located in the auxiliary furnace section maintained at 400-425°C.<sup>14</sup> If there are no other halogens but if there is sulfur, the silver should be in the same position but maintained between 500 and 550°C.,<sup>5,12</sup> because this temperature is necessary to remove completely oxides of sulfur. If other halogens and sulfur both are present, the silver must be in the principal furnace section, replacing the platinum contact, and then the furnace must not be heated to more than 900°C. However, this temperature appears to be high enough to give complete combustion of this type of material. If sulfur is present and a differential halogen determination is to be made, see Step 5.

If metals are present they will interfere by the retention of fluorine. However, in some compounds when sulfur or other halogens are present they will react with the metal and release all the fluorine.

Acids resulting from the combustion of nitrogen are not removed and they interfere with the determination.

## REMARKS

Gelatinous silica is deposited on the walls of the receiver. The gel may be sufficiently removed in several ways: 1) by agitating with water and sea sand, 2) by dissolving with 0.1N hydrofluoric acid or 50% potassium hydroxide, or 3) by exploding it from the surface by heating the moist gel sharply.

If the tube filling is allowed to protrude about 2 cm. from the furnace section into the combustion section toward the sample, the tendency of very volatile substances to explode is reduced greatly.<sup>15</sup>

The difference in the expansion coefficients of quartz and borosilicate glass must be taken into consideration in joining and separating the F joints connecting them. A 5-minute preheating (during which time

the sample can be weighed) before attempting a tight joint seems sufficient.

The platinum contacts should be etched with aqua regia each time they are handled. More frequent treatment appears unnecessary.

If the silver is positioned in the principal furnace (B) section, the life of the combustion tube is shortened because the silver halides and silver sulfate fuse with the quartz. Hence, if possible, it is advisable to locate it in the more temperate auxiliary furnace (C) section.

Previously, a combustion temperature of 900°C. was recommended,<sup>2</sup> but since then some highly fluorinated substances have been encountered which give consistently low and variable results at this temperature. These are: some ethers, biphenols, benzoic acids, and substances which on oxidation may go through the benzoic acid stage, such as acetophenones. The above appear to yield at 1150°C.

The sintered glass disk of the Grote-type receiver (E) has a tendency to stop up with use. A thin layer of acid-washed filter paper slurry can be laid down on the impinging (under) surface before the receiver is charged with water, and this layer presents a fresh surface for each determination. If the layer becomes plugged, the spray trap (F) can be disconnected from the vacuum line long enough to apply pressure with an aspirator bulb to free the stoppage. After this the spray trap is again connected to the vacuum line and the determination can be completed.

Polymers tend to decompose rapidly to lower-boiling fragments. To control their combustion, a dry-ice and acetone bath (fig. 3) can be placed between the sample and the combustion furnace. After the sample is volatilized, the bath is removed and the combustion is completed after the cooled section has warmed gradually to room temperature.

Liquids boiling at or below room temperature are handled similarly to polymers. After the sample is frozen in the

capillary in the combustion tube, the tip is broken off with pressure from a spatula.

A fine immersion tip may be drawn from borosilicate glass and attached to the burette. This tip will allow adding smaller increments of alkali in the titration. The solution which has been standing in the tip between runs should be purged by running a small amount of fresh solution through the tip.

Boron-free and carbonate-free standard alkali is most easily prepared by the dilution of 5N sodium hydroxide solution which is stored in a boron-free glass bottle and which is preserved carbonate-free by the addition of an excess of barium chloride.

A new combustion tube and the quartz chips for the filling should be cleaned with the usual chromic acid solution. In addition, a brief etching with 0.1N hydrofluoric acid, followed by a thorough flushing with water, improves the quality of the first few determinations.

## STEP 2—HALOGEN DETERMINATION BY DIRECT ABSORPTION

### METHOD

In this determination the sample is burned in an atmosphere of oxygen and the products of the combustion are swept over previously weighed, clean silver where they are absorbed quantitatively.<sup>14</sup> The gain in weight of the silver measures the total halogen content, excluding fluorine.

### EQUIPMENT

The complete fluorine combustion train (Step 1).

### REAGENTS

Concentrated ammonium hydroxide.  
Potassium cyanide (2%).

### PROCEDURE

The procedure is identical, and may be done concurrently, with that for determining fluorine (Step 1). The silver packed in the perforated platinum cylinder (fig. 2), or wrapped in platinum gauze, is cleaned of silver chloride and silver bro-

mide by soaking it for two minutes in concentrated ammonium hydroxide; or if silver iodide is present, alone or in combination with the others, the silver may be cleaned with a 2% solution of potassium cyanide. After this, the silver is well rinsed with distilled water and placed in position in the auxiliary furnace section of the combustion tube to acclimate at 400-425°C. for 10 minutes. It is then removed, allowed to cool upon a metal block by the balance, and weighed after 10 minutes. Then it is returned to the combustion tube and the procedure carried out as in the fluorine determination.

When the combustion and sweeping are completed, the silver is removed and weighed as before. The gain in weight represents the total halogen content except fluorine.

### CALCULATION

$$\frac{\text{Gain in weight}}{\text{Sample weight}} \times 100 = \% \text{ Halogen}$$

### INTERFERENCE

Some metals interfere through the formation of halide salts.

Sulfur also interferes (see Remarks, Step 1).

### REMARKS

Even though there is no fluorine in the sample, it is advisable to use the receiver because of its advantages in controlling the rate of flow of the oxygen and in carrying out the combustion under pressure. The water in the receiver may be used for a qualitative test for unretained halogen.

Greater accuracy is obtained by encasing the silver section in a perforated platinum cylinder or in platinum gauze, which prevents accidental loss of silver halide through abrasion.

The temperature is important in the absorption.<sup>14</sup> Below 400°C. the capacity of the silver is low, and above 425°C. decomposition of the silver halide takes place. Between these limits, the silver section appears to be able to remove 5 or 6 mg. of halide before cleaning is necessary.



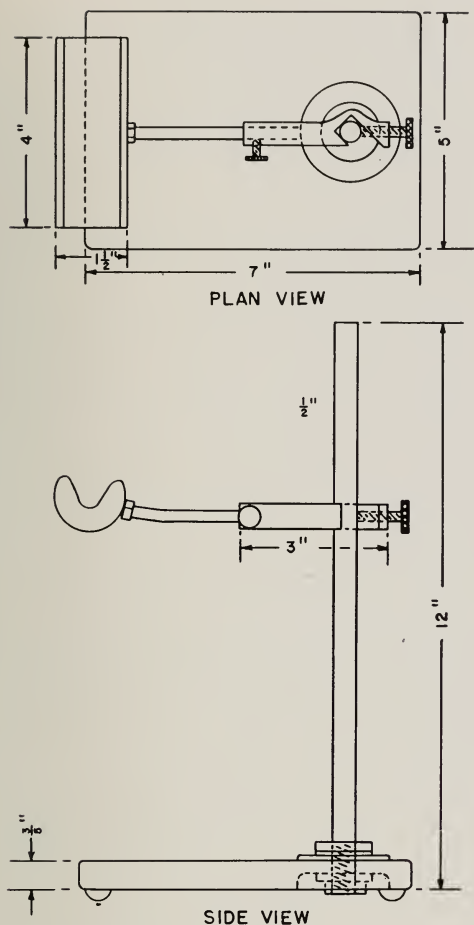


FIG. 3.—Dry-ice and acetone bath.

This direct absorption procedure does not give the high accuracy usually associated with argentometric procedures, but it does serve a purpose. For example, substances which do not contain hydrogen are often resistant to oxidation with concentrated nitric acid and cannot be analyzed by a Carius wet combustion procedure. Not all hydrogen-free substances are resistant, as one of the substituents may be labile under the digestion conditions. However, for a compound which resists acid digestion, a dry combustion method (see Step 3 also) is very convenient. Also, for polymers which may not be consistently uniform, it is very desirable to obtain a fluorine-halogen ratio on the same sample.

### STEP 3—ARGENTOMETRIC HALOGEN DETERMINATION

The argentometric method of gravimetrically determining organically bound halogen is classical, and properly carried out it is by far the most accurate method available to the microanalytical chemist for this purpose.

#### CATALYTIC COMBUSTION METHOD

This procedure is well covered in available texts.<sup>8,12,17,11</sup> It involves the destruction of the organic material by combustion in oxygen, the absorption of the halogen combustion products in an appropriate reagent, and finally the determination of the halogen gravimetrically as the insoluble silver salt.

#### EQUIPMENT

The complete fluorine combustion train (Step 1) without silver. The usual equipment for collecting, drying, and weighing the silver halide precipitate.

#### REAGENTS

Sodium carbonate solution (25 g./100 ml.) halogen-free.

Ammonium bisulfite solution, halogen-free (see Remarks).

Superoxol, halogen-free.

Concentrated nitric acid, A.C.S. reagent grade.

Nitric acid, 1 to 100, halogen-free.

Silver nitrate solution (5 g./100 ml.).

Ethanol, 95% (or SD 3A), halogen-free, filtered.

Potassium iodide solution (30 g./70 ml.), filtered.

#### PROCEDURE

The receiver is charged with 2 ml. of the sodium carbonate solution and 0.5 ml. of ammonium bisulfite. The sample is burned as in the fluorine determination but with no silver in any portion of the combustion tube.

After the combustion and sweeping, the receiver solution is transferred with distilled water<sup>18</sup> to a precipitation vessel.

This solution must be maintained at room temperature<sup>10</sup> with continuous stirring throughout the precipitation of the halide or halides. One ml. of 30% Superoxol is added, followed in approximately 30 minutes by 1 ml. of concentrated nitric acid. The walls of the vessel are washed down with 1-to-100 nitric acid and the halide or halides are precipitated by adding slowly 2 ml. of 5% silver nitrate solution. This is allowed to stand for five minutes and then the precipitate is digested in a hot-water bath for at least one-half hour.

The precipitate is transferred to the filter with 1-to-100 nitric acid, water, and alcohol and is weighed after drying at 120°C.

Because of contamination with silica, the weight of the silver halide must be determined by difference. To accomplish this, it is dissolved from the filter with 1 ml., or more if necessary, of the filtered potassium iodide solution.<sup>11</sup> This will require about one hour, after which the filter is washed in turn with potassium iodide solution, water, 1-to-100 nitric acid, water, and alcohol. After drying at 120° the filter is again weighed, the loss in weight being the weight of the silver halide.

#### CALCULATION

$$\frac{(\text{AgX}) (\text{Factor}) (100)}{\text{Sample Weight}} = \% \text{ Halogen}$$

#### REMARKS

Iodine crystals and bromine may appear on the walls in the cool upper portion of the receiver, but they can be driven into the liquid by gently warming the vessel during the flushing period.

Ammonium bisulfite is used to reduce halates which may be formed, particularly when mixtures of halides are present. Superoxol is added to destroy the excess bisulfite which would precipitate silver and to assure complete reduction of the halates which may have survived the alkaline bisulfite treatment.

The ammonium bisulfite solution can be prepared by bubbling a slow stream of halogen-free sulfur dioxide through cold concentrated ammonium hydroxide until

the ammonia odor is reduced to a minimum. It must be kept cool during the absorption.

The silver halide must be weighed by difference as it is contaminated with silica resulting from the reaction of the sodium carbonate solution with the glass receiver. Fluorine does not form an insoluble silver salt, but it reaches the receiver as silicon tetrafluoride which will contribute silica to the precipitate.

Decomposition by the Carius wet combustion method<sup>8,11,12,17</sup> may be used for the argentometric determination, but completely fluorinated compounds are often resistant to wet oxidation (see Remarks, Step 2). Fluorine will not interfere if the silver halide is weighed by difference.<sup>8,11</sup>

#### STEP 4—DETERMINATION OF IODINE IODOMETRICALLY

The iodometric method of determining iodine is well known and is generally well covered in available textbooks<sup>8,11,12</sup> and elsewhere.<sup>18,6</sup>

#### METHOD

The sample is burned in oxygen, and the iodine, after absorption in an appropriate solution, is oxidized to iodic acid. Following destruction of the excess oxidizing agent, the iodic acid is determined iodometrically.

#### EQUIPMENT

The complete fluorine combustion train without silver.

Burette, 5 ml. capacity, at least 0.050 ml. graduations.

Iodine titration flasks, 250 ml.

#### REAGENTS

Sodium acetate in glacial acetic acid (10 g./100 g.).

Aqueous sodium acetate (20 g./100 ml.).

Bromine, reagent grade, iodine-free.

Formic acid, reagent grade, 80-100%.

Sodium thiosulfate solution 0.01N.

Potassium iodide, reagent grade, iodate-free.

Sulfuric acid (1 to 9).

Amylose starch indicator solution.

## PROCEDURE

The procedure is identical with that of the fluorine determination (Step 1) except that the receiver is charged with 2 ml. of the acetic acid-sodium acetate reagent containing a few drops of bromine.

After the combustion and sweeping are complete, the contents of the receiver are transferred to an iodine titration flask first by washing with 5 ml. of the aqueous sodium acetate solution containing a little bromine and then by washing with water. The excess bromine is destroyed by adding several drops of formic acid. Gentle shaking will wash down the walls and also remove bromine vapor from the air above the solution. More formic acid is used if necessary to remove all the bromine color. After this has been allowed to react for five minutes, 2 ml. of freshly prepared potassium iodide solution is washed in around the stopper and, after thorough mixing, this is followed by 3 ml. of the dilute sulfuric acid, added in the same way. After shaking gently again, the reaction is allowed to go to completion for five minutes before titration with 0.01N sodium thiosulfate solution.

## CALCULATION

$$\frac{V_{\text{Na}_2\text{S}_2\text{O}_3} \times N_{\text{Na}_2\text{S}_2\text{O}_3} \times \text{Mil. Eq.} \times 100}{\text{Sample Weight, mg.} \times 6} = \% \text{ I}$$

## REMARKS

If it is preferred, a Carius iodometric determination of iodine in organic compounds may be substituted for the above combustion procedure.<sup>8,19</sup>

If chlorine is also present, varying amounts of the bromine may be oxidized to bromate, which is not destroyed by formic acid. Without a catalyst, small amounts of bromate react so slowly with potassium iodide that it does not seem to interfere<sup>7</sup> if the titration is carried out fairly rapidly.

## STEP 5—DIFFERENTIATION BY INTERPRETATION

## FLUORINE AND ONE HALOGEN

Through the proper interpretation of the information obtainable in the preceding four steps a complete differentiation can be made, and the percentage of each individual halogen can be determined. If the other halogens are known, identification may not be required, but we will consider that we are dealing with unknown substances.

The simplest combination is fluorine and one halogen:

Fluorine by Step 1.

Halogen gravimetrically by Step 2 (unidentified).

Halogen argentometrically by Step 3.

*Indications.*—If the argentometric determination (Step 3) calculated as chlorine is the same as the percentage of total halogen found by direct absorption (Step 2), the halogen is chlorine. The same applies to iodine.

However, a fortuitous combination of chlorine and iodine could simulate the proper weight of silver halide for bromine. Thus in order to confirm bromine alone it will be necessary to demonstrate the absence of iodine by Step 4.

## FLUORINE AND MORE THAN ONE HALOGEN

A more difficult combination is fluorine and more than one halogen:

Fluorine by Step 1.

Halogen gravimetrically by Step 2.

Halogen argentometrically by Step 3.

Iodine iodometrically by Step 4.

*Indications.*—If the result of Step 3, calculated as chlorine, is less than that of Step 2 and if the two steps are not in agreement when the former is calculated as chlorine, bromine, or iodine, the calculations are:

$$\text{Factors } \frac{\text{Cl}}{\text{AgCl}} = 0.2474 \quad \frac{\text{AgCl}}{\text{Cl}} = 0.042$$

$$\frac{\text{Br}}{\text{AgBr}} = 0.4255 \quad \frac{\text{AgBr}}{\text{Br}} = 2.350$$

$$\frac{\text{I}}{\text{AgI}} = 0.5405 \quad \frac{\text{AgI}}{\text{I}} = 1.850$$

$$\left( \frac{\text{Cl}}{\text{AgCl}} \right) \left( \frac{\text{AgCl}}{\text{Cl}} - \frac{\text{AgBr}}{\text{Br}} \right) = .4186$$

$$\left( \frac{\text{AgI}}{\text{I}} \right) \left( \frac{\text{Cl}}{\text{AgCl}} \right) = .4577$$

No sample weight will be used in the differential calculations as the sample weight will be considered to be unity. Unless otherwise indicated the term "Step 3" refers to the percentage of halogen calculated as chlorine.

CALCULATIONS

a) Iodine absent by Step 4:

$$\frac{(\% \text{ Step 2} - \% \text{ Step 3})}{\left( \frac{\text{Cl}}{\text{AgCl}} \right) \left( \frac{\text{AgCl}}{\text{Cl}} - \frac{\text{AgBr}}{\text{Br}} \right)} = \% \text{ Br}$$

$$\% \text{ Step 2} - \% \text{ Br} = \% \text{ Cl}$$

b) Iodine present by Step 4:

$$\% \text{ Step 2} - \% \text{ Step 4} = \% \text{ of other halogen.}$$

$$\text{IF } \left[ \left( \frac{\% \text{ Step 3}}{\frac{\text{Cl}}{\text{AgCl}}} \right) - \left( \frac{\% \text{ Step 4}}{\frac{\text{I}}{\text{AgI}}} \right) \right] \frac{\text{Cl}}{\text{AgCl}} = \% \text{ of other halogen}$$

then the other halogen is chlorine.

$$\text{BUT IF } \left[ \left( \frac{\% \text{ Step 3}}{\frac{\text{Cl}}{\text{AgCl}}} \right) - \left( \frac{\% \text{ Step 4}}{\frac{\text{I}}{\text{AgI}}} \right) \right] \frac{\text{Br}}{\text{AgBr}} = \% \text{ of other halogen}$$

then the other halogen is bromine.

If neither equation is true, then both

chlorine and bromine are present and the equation becomes:

$$\frac{(\% \text{ Step 2} - \% \text{ Step 4}) - \left( \% \text{ Step 3} - \% \text{ Step 4} \cdot \frac{\text{AgI}}{\text{I}} \cdot \frac{\text{Cl}}{\text{AgCl}} \right)}{\left( \frac{\text{Cl}}{\text{AgCl}} \right) \left( \frac{\text{AgCl}}{\text{Cl}} - \frac{\text{AgBr}}{\text{Br}} \right)} = \% \text{ Br}$$

$$\% \text{ Step 2} - (\% \text{ Br} + \% \text{ I}) = \% \text{ Cl}$$



## REMARKS

If sulfur is present it will interfere with Step 2. In this event, instead of making the differential calculations on the basis of the halogen-silver halide ratio, it will be necessary to make it on the silver-silver halide ratio, the silver being determined by electrolysis<sup>13</sup> from the silver halide obtained in Step 3.

In actual practice, unless all four elements are present, it usually is not necessary to do all four analyses; and it is rarely necessary to do all the calculations because inspection usually will indicate which elements are probably present; but if needed, the mechanism is available.

## PART II

### MICRODETERMINATION OF CARBON, HYDROGEN, NITROGEN, AND SULFUR IN ORGANIC COMPOUNDS CONTAINING FLUORINE

To complete the coverage of analysis for organic fluorine compounds which have often been troublesome to analysts,<sup>1,9</sup> the following brief discussion of methods for determining carbon, hydrogen, nitrogen, and sulfur is included. Although there will be procedural variations from laboratory to laboratory, the basic principles will be identical. Therefore the more common determinations and manipulations are not described in detail; however, where they are important, certain modifications and descriptions are indicated.

#### CARBON AND HYDROGEN

##### METHOD

The organic substance is burned with oxygen in a quartz, or Vycor, combustion tube. The tube filling will assist the combustion and will either remove or modify all other products of the combustion so that they will not interfere with the subsequent differential absorption of the water and carbon dioxide.<sup>8,11,12,17</sup>

##### EQUIPMENT

The conventional carbon-hydrogen combustion train is used with a modified Silbert and Kirner<sup>16</sup> combustion tube filling. The principal variation of the Silbert and Kirner tube filling is the addition of a lead oxide section which, in addition to its particular use (for P, As, Sb, and Bi), appears to serve admirably in cracking very stable halogenated substances. The modification includes relocating the lead oxide section in another part of the combustion furnace where the temperature is more easily controlled.<sup>4</sup>

##### REAGENTS FOR THE COMBUSTION TUBE FILLING

Copper oxide wire form, reagent grade, is broken into approximately 2 mm. lengths

using a mortar and pestle. All that passes through a 40-mesh sieve is discarded, and the remainder is wet with glacial acetic acid and washed by decantation with distilled water. After ignition to dull redness and cooling while protected from dust, it is ready for use in the tube filling.

Lead dioxide pellets, reagent grade, are commercially available, but better results are obtained if the pellets are freshly prepared in the laboratory. Enough reagent lead dioxide to make a 5 mm. layer on the bottom of a 250 ml. beaker is made into a slurry with concentrated nitric acid, heated on a steam bath for about one hour, and then washed by decantation until acid-free to litmus paper. After the final decantation it is dried at 80°C. until it is firm enough to be broken into lumps about 2-3 mm. square. Heating beyond this point tends to change the color from the normal black to mahogany and is not advisable.

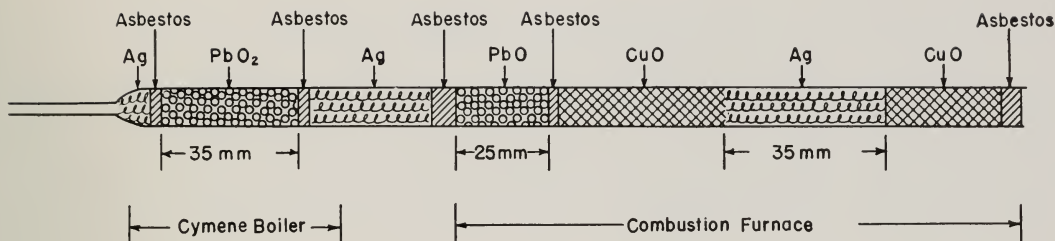
Lead oxide pellets, reagent grade, are prepared by shaking lead dioxide pellets in a porcelain crucible heated just short of redness over a Fisher or Tirril burner. When heated, the pellets gradually turn to orange red or pale chocolate, and become yellow or orange when cool.

Silver ribbon, reagent grade, is ignited gently by passing repeatedly through a flame to remove organic surface impurities just before inserting into the combustion tube.

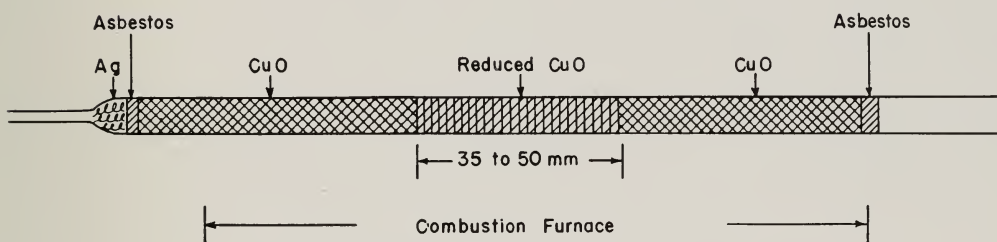
Asbestos fiber, Gooch, acid-washed, is ignited strongly just before inserting into the combustion tube.

##### COMBUSTION TUBE FILLING

The combustion tube is packed in the accustomed manner using the arrangement shown in figure 4.



CARBON-HYDROGEN COMBUSTION TUBE



DUMAS NITROGEN COMBUSTION TUBE

FIG. 4.—Combustion tubes.

## REMARKS

Lead dioxide begins to fuse with quartz or Vycor at about 725-750°C. so careful control of the temperature is important. Using this tube filling, nearly all organo-fluorides appear to yield to combustion at 700°C., which is the temperature recommended for general use. Occasionally, however, very stable substances will require increasing the temperature to 725°C. Therefore, if low and variable carbon values are obtained at the regular temperature it is advisable to increase the temperature and repeat the analysis.

Because of the stability of organic fluorine compounds, often combined with high volatility, unusual precautions must be taken occasionally to assure a uniform, slow combustion with a high oxygen ratio. (See Part I, Step 1.) As it is not advisable to increase oxygen flow beyond the usual

5-8 cc. per minute, it is necessary to control the combustion instead.

## SULFUR

Fluorine does not interfere with the gravimetric Carius wet combustion method of determining sulfur if the procedure includes evaporation to dryness with hydrochloric acid and sodium chloride.<sup>11</sup> The filter apparatus according to A.C.S. specifications<sup>3</sup> and the evaporation apparatus made to our specifications by the Arthur H. Thomas Co. are recommended.

## NITROGEN

Fluorine does not interfere with the Dumas nitrogen determination. The combustion is made at 700°C. using the combustion tube filling illustrated in figure 4. To our knowledge, no compound has failed to yield to these conditions.

## RESULTS OF ANALYSES

Sample Number	Molecular Formula	Carbon-%		Hydrogen-%		Fluorine-%		Chlorine-%		Bromine-%		Iodine-%	
		Theory	Found	Theory	Found	Theory	Found	Theory	Found	Theory	Found	Theory	Found
Fl-640	C <sub>7</sub> H <sub>5</sub> OF <sub>3</sub>	51.86	51.94	3.11	2.95	35.16	35.08	—	—	—	—	—	—
Fl-674	C <sub>7</sub> H <sub>4</sub> O <sub>2</sub> F	53.18	53.32	2.55	2.44	24.04	24.01	—	—	—	—	—	—
Fl-679	C <sub>8</sub> H <sub>5</sub> OF <sub>3</sub>	55.18	55.12	2.89	2.94	32.74	32.58	—	—	—	—	—	—
Fl-696	C <sub>14</sub> H <sub>12</sub> O <sub>2</sub> F <sub>2</sub>	67.19	67.08	4.84	4.63	15.19	15.00	—	—	—	—	—	—
Fl-682 701	C <sub>8</sub> H <sub>6</sub> OF <sub>2</sub>	61.54	61.51	3.87	3.70	24.34	24.39	—	—	—	—	—	—
Fl-702	C <sub>12</sub> H <sub>8</sub> O <sub>2</sub> F <sub>2</sub>	64.87	64.92	3.63	3.62	17.10	17.04	—	—	—	—	—	—
Fl-662	C <sub>7</sub> H <sub>4</sub> ClF <sub>3</sub>	46.56	46.70	2.23	2.37	31.57	31.76	19.64	19.59	—	—	—	—
Fl-691	C <sub>7</sub> H <sub>6</sub> OClF	52.35	52.55	3.77	3.75	11.83	12.12	22.08	21.85	—	—	—	—
Fl-698	C <sub>6</sub> H <sub>4</sub> OClF	49.17	48.93	2.75	2.66	12.96	13.15	24.20	23.98	—	—	—	—
Fl-703	C <sub>7</sub> H <sub>6</sub> OClF	52.35	52.42	3.77	3.61	11.83	11.96	22.08	21.89	—	—	—	—
Fl-690	C <sub>8</sub> H <sub>6</sub> O <sub>3</sub> BrF	38.58	38.52	2.43	2.34	7.63	7.92	—	—	32.09	32.14	—	—
Fl-684	C <sub>7</sub> H <sub>6</sub> OBrF	41.00	41.19	2.95	2.83	9.27	9.07	—	—	38.98	39.29	—	—
Fl-693	C <sub>6</sub> H <sub>5</sub> OIF	30.28	30.23	1.69	1.78	7.98	8.08	—	—	—	—	53.33	53.75
Fl-685	C <sub>7</sub> HO <sub>6</sub> IF	33.36	33.41	2.40	2.41	7.54	7.68	—	—	—	—	50.36	50.69
Fl-784	C <sub>7</sub> H <sub>2</sub> F <sub>3</sub> ClBrI	21.81	21.84	0.52	0.58	14.79	14.88	9.20	9.11	20.74	20.95	32.93	32.87
Fl-787	C <sub>6</sub> HF <sub>2</sub> ClBrI	20.39	20.47	0.29	0.30	10.75	10.79	10.03	10.05	22.61	22.77	35.92	35.81

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